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Transformation of CO_2 by using nanoscale metal catalysts: cases studies on the formation of formic acid and dimethylether

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The valorization of CO_2 has gained increasing interest in the scientific and industrial communities during the last decades with intensive research devoted to CO_2 capture, sequestration and utilization. This is because the greenhouse gas emission has become a serious concern to face the global climate change and that efficient solutions are required to reduce the carbon footprint. Up to now the chemical transformation of CO_2 into fuels and target molecules has been mainly investigated by using molecular catalysts. However, the ability of heterogeneous catalysts or nanomaterials for this catalysis has been recently explored and promising results achieved in the production of formic acid (FA) and dimethylether (DME) from CO_2 with nanoscale metal catalysts. Relevant examples will illustrate the high potential of this class of catalysts that could offer new solutions for the selective transformation of CO_2 toward fuels and high added value chemicals in the future.

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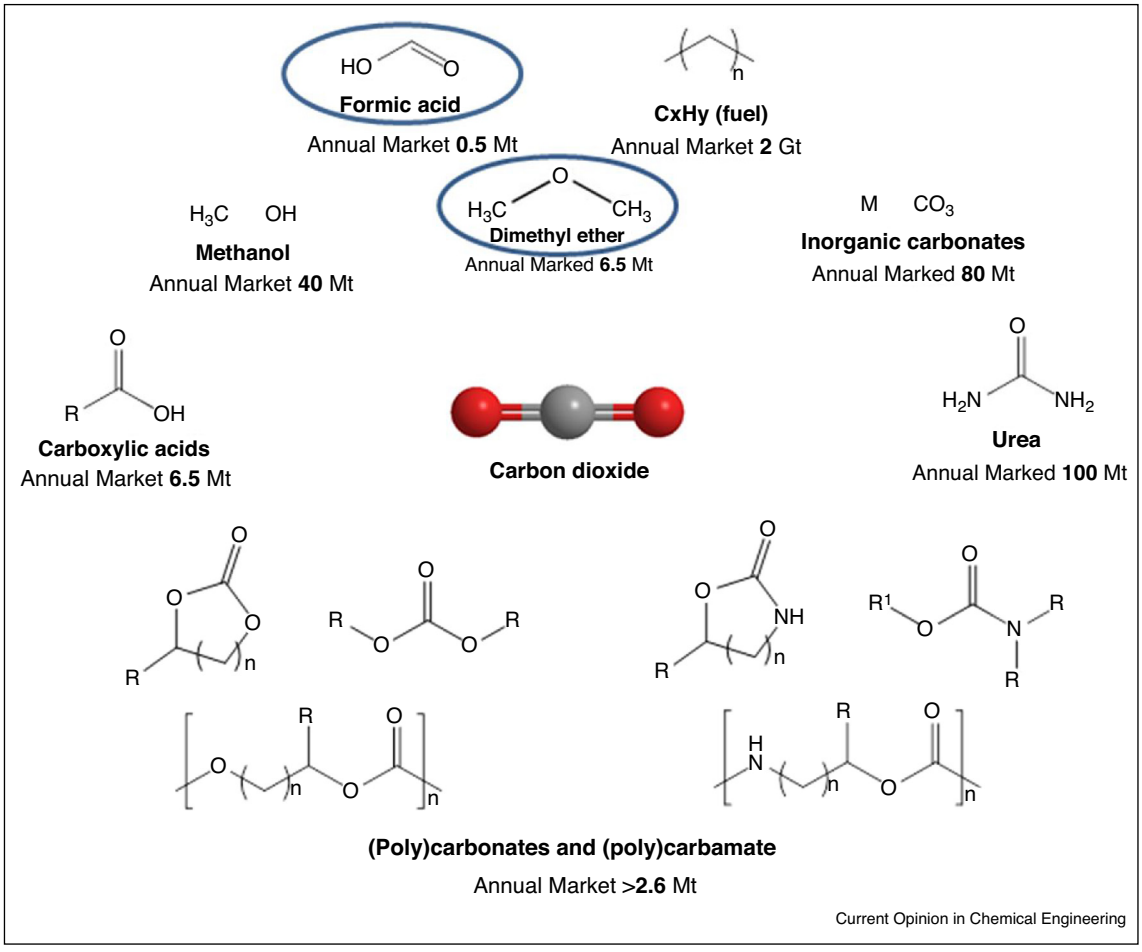
Introduction

CO_2 capture, storage and utilization are a focus of intensive research today, given greenhouse gas emission (where CO_2 takes a major place) has become a serious concern in front of the global climate change [1•], as illustrated by the numerous international actions from governments, academia and industries over the past decades.

If major global efforts made in the attempts to reduce the carbon footprint focus on the long-term storage of CO_2, more efforts are required in order to develop technologies for the valorization of CO_2 as a 'raw material'. Indeed, CO_2 is a cheap, non-toxic, abundant, reproducible and cost efficient chemical that can be used as carbon source for the synthesis of fuels and various chemicals that are today mainly produced from non-renewable resources [2]. Converting CO_2 has thus a huge appeal, not only due to the carbon fixation potential, but also because it may complement current chemical industry by providing value-added products (see Figure 1 for chemicals that may be obtained from CO_2 and their carbon capture capability) but today there are only nascent strategies. It is noteworthy that the products described in Figure 1 are currently not (mainly) produced from CO_2 due in part to technical challenges and that major scientific breakthroughs are needed to make the CO_2 route economically viable. A recent review reports an analysis of the state-of-the-art of synthetic methodologies and CO_2-involving processes with the assessment of their life cycle in order to evaluate the potential to reduce the environmental footprint relative to the current petrochemical value chain [3••]. The authors tried to identify opportunities by exploiting CO_2 as a novel feedstock that avoids the utilization of fossil resource in transition toward more sustainable future production. The motivation to develop CO_2-based chemistry does not have to depend primarily on the amount of CO_2 emissions but has to be stimulated by the significance of the relative improvement in carbon balance and other critical factors defining the environmental impact of chemical production in all relevant sectors in accord with the principles of green chemistry.

One main issue with CO_2 is that it displays a high thermodynamic stability [4]. CO_2 transformation thus requires developing efficient catalytic systems [5] that offer a good balance between the energy needed and the gain obtained. Significant progress has been made in the direct electrochemical reduction of CO_2 to fuel molecules (like formic acid, methanol or methane) which could be a viable strategy if powered by a carbon-neutral electricity using nanoscale catalysts (Pt, Co, Ni, ZnO) [6]. But one main issue with this approach is the absence of stable catalysts that can enable the CO_2 reduction reaction at low overpotential and high selectivity over the hydrogen evolution one. Photocatalytic conversion of CO_2 based on the use of metal-doped semiconductors

Figure 1



Potential chemicals from CO_2 transformation.

for harnessing the energy from sunlight is another domain of increasing interest, but improvement is still needed to avoid the use of sacrificial electron donors. As for the chemical reduction of CO_2 by using hydrogen, it remains a significant challenge. This process is thermodynamically unfavorable, being the net reaction between gaseous H_2 and CO_2 to liquid HCOOH endoergonic due to the strong entropic contribution ($\Delta G^0_{298} = 32.9\,kJ\,mol^{-1}$). To render the transformation of CO_2 to formic acid (or formates) feasible in practice, the thermodynamic equilibrium has to be disturbed by secondary reaction or molecular interaction. Common strategies are by esterification (e.g. reacting formic acid/formates with methanol to yield methyl formate followed by reacting with amines to yield formamides) or simply neutralization with a base such as ammonia and triethylamine or alkali/alkaline earth bicarbonates. Moreover, the chemical equilibrium of CO_2/bicarbonate (HCO_3^-)/carbonate (CO_3^{2-}) is influenced by many parameters, such as temperature, CO_2 pressure, nature of base, and solution pH.

With increasing worldwide interests and investments toward the valorization of CO_2, increased examples of producing chemicals from CO_2 in both scientific and industrial communities have emerged in recent years. A very pronounced case is the conversion of CO_2 into methanol, which is most commonly produced from natural gas. The world's first industrial process that uses CO_2 as a feedstock for the synthesis of methanol was implemented by Mitsui Chemicals in 2009. This demonstrates the feasibility of creating value from CO_2 through the generation of innovative novel technologies and is a new answer to the CO_2 dilemma. Apart from methanol, formic acid (FA; HCOOH) and dimethylether (DME; $(CH_3)_2O$) are currently among the top in the list of chemicals that CO_2 can offer. Hydrogenation of CO_2 into FA provides the simplest and most direct solution for the long desired chemical loop for hydrogen storage using CO_2. While FA is not a perfect hydrogen storage vector due to its relatively small hydrogen content (4.4 wt%; 53 g L^{-1} hydrogen at room temperature and ambient pressure), it is presently still one of the best among liquid storage and

transport media for H_2. DME is another highly interesting chemical that can be generated by direct CO_2 hydrogenation. DME is superior compared with petro diesel in diesel engines, since it is virtually free from sulfur and aromatics, thus emitting less CO, SO_x and particulates.

In the past decade, relevant examples in the use of nanoscale metal catalysts for the production of FA and DME from CO_2 have been reported. They illustrate well the high potential of this class of catalysts for these difficult transformations.

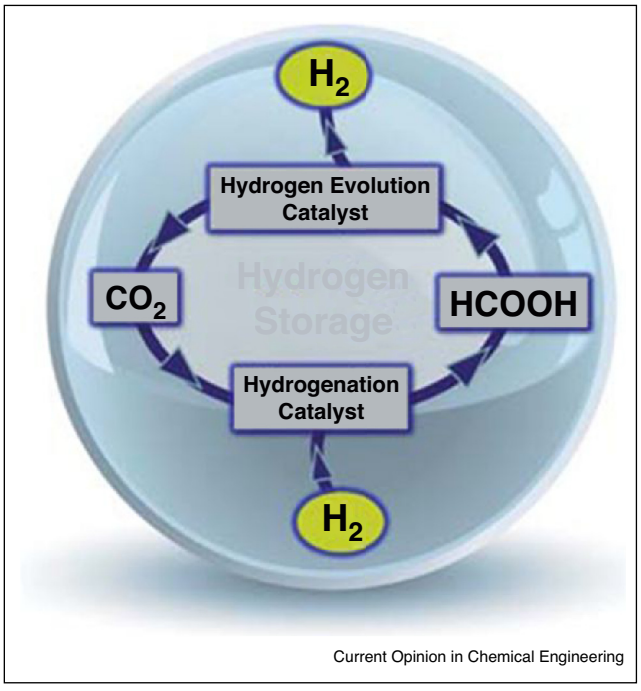
Transformation of CO_2 into formic acid

Formic acid is a valuable basic chemical, being largely used as a preservative, an antibacterial, an insecticide agent and also as a de-icing agent. Numerous applications are found in leather and tanning industries, textile and rubbers markets, deicing of roads, silage preservation and animal feed or medical sector, etc. FA plays also a major role in synthetic chemistry as an acid, a reductant and a precursor for syntheses. Moreover, FA is established as a liquid 'hydrogen-carrier' and thus as a promising alternative for chemical energy storage (Figure 2) [7].

With an annual production capacity of >300 kt of FA compared to global 800 kt, BASF is the world leader market followed by BP and Eastman. Even if it can be obtained by oxidation of biomass, the most common process to produce FA relies with the formal carbonylation of water via methyl formate or methyl formamide. It is a two-step procedure: methanol reacts with CO leading to methyl formate (typical conditions: a base catalyst, 80°C, P_{CO} = 45 bar) which is then hydrolyzed in FA and methanol (autocatalyzed by FA itself) [3••]. It is demonstrated that the proton transfer to the base drives the reaction. Another important issue in this process is the separation of FA from the reaction mixture that requires a dedicated extraction as well as an economic and energetic cost [2]. Given the above the direct catalytic reduction of CO_2 offers a highly attractive route to get FA from an abundant raw-material by providing a 'shortcut' to the desired product. However, this appealing approach requires to have at disposal appropriate catalysts able to advantageously reduce CO_2 to HCOOH and, if targeting FA as a hydrogen carrier, catalysts able to selectively decompose FA to release CO-free H_2.

Direct hydrogenation of CO_2 into FA with homogeneous catalysts has been extensively studied and is well-documented with several reviews where both the tremendous advances in the field and the scientific and technological challenges that remain to overcome are highlighted [2,3••,8–10]. Numerous and various active molecular complexes in organic solvent, water, glycerol, ionic liquids or sCO_2 conditions at temperature in the range RT-120°C are claimed. They contain mostly Ru, Rh or Ir but catalytic systems involving non-noble metals like Fe, Co, Ni and Cu are also reported. Efficient complexes for example display electron-rich metal centers (using electron-donating ligands) and are able to activate H_2 under the form of hydrides and to transfer these hydrides to CO_2, for some of them under mild conditions. Described complexes mainly contain phosphanes which can be sulfonated for water solubility purpose, but carbenes or pyridine derivatives are used also. Ligands and the reaction medium are known to play a crucial role (for instance water can favor producing FA). Apart from H_2, other reducing agents can be used namely, hydroboranes or hydrosilanes [5,11]. The use of glycerol as hydrogen donor has been also reported, a reaction of high interest since this allows to convert two waste materials into useful products [12]. In spite of the excellent catalytic performances (both in terms of activity and selectivity) achieved by several homogeneous catalysts, they are still far from what would be desired from an industrial standpoint, as the result of the low catalyst concentrations often used in homogeneously catalyzed processes [13••]. The immobilization of homogeneous catalysts at the surface of supports (mainly, silica-based and polymer-based materials or porous organic polymers) has also been investigated because heterogenized complexes allow to circumvent the difficulties linked to the separation and recovery of the catalyst, another issue in homogeneous catalysis [13••,14•]. By combining the desired properties of tunable, well-defined, highly active catalytic sites of a homogeneous system with a heterogeneous one, this approach

Figure 2



Schematic representation of the CO_2/HCOOH hydrogen storage system.

helps with the catalyst handling and also leads to higher activity per unit volume.

In the opposite, despite the old works involving Pd black [15] and Ni-Raney [16] and their practical advantages for continuous operation and product separation, the development of heterogeneous catalysts for the direct hydrogenation of CO_2 lags significantly behind that of homogeneous catalysts [13••,14•]. However, the number of examples is increasing since recently in particular for supported nanoparticulate metal catalysts.

For bulk metal catalysts, apart from the use of Pd black and Raney-Ni as previously cited, three papers report on the formation of FA from a mixture of H_2/CO_2 gases on Au [17], Pd [18] and Ru [19] catalysts with very poor activities. In the later case, supported nanoparticles have been observed but they are not well-defined. Compared to bulk materials which display poor active surface and are thus economically inefficient for high-scale catalytic processes, nanoscale catalysts are well-known as being highly dispersed metals that provide high numbers of active sites [20]. However, despite the huge progress made in nanochemistry and nanotechnology during the past 20 years and the fact that they were studied for the formation of FA from carbonates (mainly with Pd), only a few examples of supported metal catalysts at the nanoscale are reported for the direct hydrogenation of CO_2, mainly involving Au, Pd and Ru. If in terms of catalytic performances the described systems are quite far from those of heterogenized molecular complexes, they present interesting behaviors that remind those of supported homogeneous catalysts and thus merit to be more explored. Most of supports used are inorganic ones like carbon or inorganic oxides materials, and the crucial role of metal–support interaction in the CO_2 hydrogenation activity is demonstrated.

So, colloidal Au nanoparticles (NPs) have been reported as being not active compared to supported ones and, among a range of supports tested, changing TiO_2 by Al_2O_3 allowed a twofold increase of the activity of Au NPs (TOF of 5.5 $hour^{-1}$ against 11 $hour^{-1}$, respectively), due to specific metal–support interface [21]. This relates to the ability of the support to facilitate heterolytic H_2 dissociation. This process can occur on the metal itself or on the reactive metal–support interface. Mechanistic studies highlighted the importance of M–H bonds [22,23]. A parallel can thus be made with homogeneous catalysts where the hydricity properties of the metal complexes are known to highly influence their catalytic properties.

Similarly, Pd NPs (ca. 4.4 nm) deposited onto graphitic carbon nitride (g-C_3N_4) were compared to CNT-supported Pd NPs of similar size, leading to a catalytic activity (TOF = 3.1×10^{-4} s^{-1}) that is 12 times higher on g-C_3N_4 than CNT. It is noteworthy that this study has been performed in an eco-friendly solvent, namely water, without a base additive and under mild conditions (40°C, 50 bar $H_2/CO_2 = 1$). This result shows the strong influence of the g-C_3N_4 support in comparison to CNT that derives from the high CO_2 adsorption and activation ability of g-C_3N_4 which provides activated form of carbonate or formate to Pd where H_2 is activated [24]. This illustrates also well the synergetic effect between the metal phase and the support. The same group reported on a PdNi catalyst supported onto a carbon nanotube-graphene (CNT-GR) material where a synergetic effect is observed compared to reference monometallic Pd NPs, as the result of close interaction and synergy between the two metals [25]. If the catalytic performance claimed is quite lower (TOF = 1.2×10^{-4} s^{-1}) than that of the previous Pd/g-C_3N_4 catalyst, this example highlights the interest of exploring bimetallic systems. Interestingly also, a nanocatalyst constituted of very small Pd NPs (ca. 1.7 nm) regularly dispersed onto a mesoporous graphitic carbon nitride (mpg-C_3N_4) afforded a TOF of 144 $hour^{-1}$ under ambient and base free conditions [26]. This result is comparable to values reported with heterogeneous catalysts in similar conditions. Another relevant example about Pd is a nanocatalyst made of Pd NPs (ca. 1.8 nm) regularly dispersed along the fibers of a chitin material [27]. This nanocatalyst attended a TOF value of 257 $hour^{-1}$ in water under mild conditions (60°C; 40 bar $H_2/CO_2 = 1$) thus showing the great benefit brought by the chitin support. The acetamide groups in chitin promote the distribution of Pd NPs on the surface and accelerate the hydrogenation of CO_2 due to its coordinating ability to transition metals and Lewis basic properties. Besides the good catalytic performance obtained, this work is very original as it takes advantage of coordination chemistry properties of the chitin which is issued from the biomass.

Surprisingly, while Ru complexes (including heterogenized and isolated single-atomic systems [28]) have been extensively studied and are known to be highly efficient homogeneous catalysts for FA formation, just a few examples of metal supported catalysts with Ru are available. One can cite a comparative study on the reactivity of RuNPs (ca. 6.0 nm) deposited onto TiO_2 for the hydrogenation of CO_2 to FA, in the presence or not of an ionic liquid [29]. With TOF values in the range 20–50 $hour^{-1}$ obtained at low catalyst loading this study evidences the positive effect of the IL which acts as a solvent for the reaction able to capture CO_2. Moreover, this catalytic system based on the supported ionic liquid phase principle showed a good stability over recycling. Ru NPs (size in the range 7–14 nm) formed *in situ* in ILs are also reported as effective catalysts for the formation of FA from CO_2 with high activity (TOF up to 3300 $hour^{-1}$) and a slow decrease stability after successive recycling [30]. A very recent paper relates that CO_2 can be selectively

hydrogenated either to FA or to hydrocarbons by using small RuFe NPs (ca. 1.8 nm) in ILs under mild reaction conditions (DMSO/H_2O; 60°C; 30 bar H_2/CO_2 = 2/1) and that the selectivity depends on the nature of the anion of the IL [31]. So, the formation of FA is favored in ILs containing basic anions with a remarkable TOF value of 23.5 $hour^{-1}$ whereas heavy hydrocarbons (up to C_{21}) are more produced in the presence of nonbasic anions. The composition of the metal alloy and the basicity/hydrophobicity of the IL ion pair (mainly imposed by the anion) appear to be the keypoints for the selective transformation of CO_2. First, the IL forms a cage around the NPs that controls the diffusion/residence time of the substrates, intermediates and products. Second, compared to Ru and Fe monometallic NPs, the presence of Fe in RuFe NPs has a dual effect: a positive metal dilution effect toward the formation of FA and a synergetic one for the formation of hydrocarbons. This work clearly shows that the precise design of a nanocatalyst (here a combination between metal alloy and IL support) can lead to chemoselectivity in CO_2 hydrogenation. As a last relevant example, Ru NP prepared by reduction of $RuCl_3$ in a methyl alcohol solution under solvothermal conditions showed high activity for hydrogenation of supercritical CO_2 (sCO_2) to formic acid [32]. This work which describes another catalyst at the frontier between homogeneous and heterogeneous systems opens the door toward the use of solution nanoparticles for the hydrogenation of CO_2.

In summary, to achieve an economical CO_2-mediated hydrogen energy cycle, the development of heterogeneous catalysts for hydrogenation of CO_2 to FA is a challenging and highly desirable task. Recent efforts have shown that the precise design of solution and supported nanocatalysts can lead to the chemoselective CO_2 hydrogenation into FA, making thus a parallel with studies on molecular complexes. Prospective studies with a molecular approach could allow to tune more finely the catalytic properties of nanoscale catalysts. Mechanistic details being critical to the development of improved nanocatalysts, more efforts are also required in this direction in order to achieve higher performance.

Transformation of CO_2 into dimethyl ether

Transformation of CO_2 directly into DME requires sequential hydrogenation and dehydration reactions, which necessitate the participation of both metal centers (often Cu) and acid sites. The size of Cu particles plays a significant role in methanol synthesis activity, indirectly influencing DME formation. However, the control and maintain of Cu particle size under reactive conditions is non-trivial task. Recently, La was added as an active component to decrease the reduction temperature and the crystallite size of Cu [33]. The mixed oxide Cu-Fe and Cu-Fe-La were prepared by homogeneous precipitation starting from corresponding nitrate salts, and then mechanically mixed with HZSM-5. After La incorporation, the XRD diffraction peaks of CuO are broadened and the intensities are weakened, suggesting a decrease of the CuO particle size. The H_2-reducing temperature slightly decreased for the La containing sample, highlighting improved reducibility of Cu. The activity for CO_2 conversion increased by ca. 50% whereas selectivity toward DME was improved by 300% over the modified catalyst. Interestingly, the Cu-Fe-Ce catalysts were stable on stream for 15 hours but the Cu-Fe catalyst quickly deactivated after 6 hours. Similarly, Ce was introduced into the catalyst, prepared via the homogeneous precipitation method to get Ce-Fe-Cu mixed oxide, and then mechanically mixed with HZSM-5 [34]. Again, decrease of CuO particle size was observed. Moreover, some Cu+ was identified to enter CeO_2 lattice to form a solid solution. The enhanced dispersion of Cu is beneficial for CO_2 hydrogenation.

Both CO_2 and H_2 have to be activated for DME formation. Activated H_2 (H atom on metal surface) is also critical to maintain the metallic state of Cu. In this respect, adding a second metal to facilitate H_2 activation could be advantageous. A series of Pd modified Cu-Zn-Al-Zr/HZSM-5 catalysts was prepared, which markedly enhanced the DME yield and suppressed CO formation [35]. In TPR analysis, the reducing temperature for Cu decreased sharply from ca. 200°C to ca. 160°C. In literature, it is well established that PdO is reduced by H_2 at room temperature, and subsequently dissociates H_2 molecules. Plausibly, the chemisorb H spill over from Pd to adjacent Cu phase, promoting Cu reduction. The authors argue that the addition of Pd into Cu does not only improve the formate hydrogenolysis step, which is rate-limiting, but also improves catalyst stability by preventing the oxidation of Cu by CO_2, enabling high activity and stability at low temperature.

While HZSM-5 and Al_2O_3 are the dominant solid acids used to support Cu-based NPs, effort has been directed to optimize the type and morphology of zeolites. To understand the effect of zeolite topology on catalytic property, 2-D ferrierite (FER) and 1-D mordenite (MOR) were synthesized and used as Cu-Zn-Zr nanoparticle carriers [36]. Both TEM and SEM images reveal that Cu-Zn-Cr oxide NPs with size ranging between 30 and 150 nm were well dispersed on the 2-D lamellar structure of FER. In sharp contrast, the catalyst was composed of two separated phases, that is, oxide NPs (50 nm in size) and zeolite patches, in the case of MOR as support. As expected, FER supported Cu-Zn-Zr NPs exhibited significantly enhanced activity in CO_2 conversion to DME, presumably due to the markedly facilitated mass-transfer of methanol from Cu-Zn-Zr sites to zeolite surface.

In a majority of studies, the metal and the acid catalytic centers are mechanically mixed. It appears in a recent

report that a capsule type catalyst, with Cu-Zn-Al composite nanoparticles as the core and HZSM-5 as the shell, is more active compared with the catalysts synthesized via mechanical mixing [37]. Spherical carbons, prepared by hydrothermal method from glucose aqueous solution, were used as a template to form Cu-Zn-Al NPs. After removal of carbon by calcination, these NPs were added into a sol — the HZSM-5 precursor-formed from tetraethyl orthosilicate, ultrapure water, aluminum nitrate and sodium hydroxide. Following a hydrothermal treatment, the Cu-Zn-Al NPs were packed on HZSM-5 membranes. For mechanically mixed HZSM-5 and Cu-Zn-Al particles, CO_2 conversion was 23% and the yield for DME was merely 5% at 3.0 MPa, 270°C, whereas the capsule type catalyst reached CO_2 conversion of 48.3% and DME yield of 23.4%, respectively. This work highlights the importance of engineering the interface between the Cu-based active sites for methanol synthesis and the solid acid sites for methanol dehydration.

Another approach to engineer the Cu-zeolite interface is to add a third phase between Cu and zeolite. In a recent work, $SrCO_3$ was deposited onto Cu-Zn-Al nanoparticles, before mixing with HZSM-5 [38]. The CO_2 conversion and DME yield steadily increased when $SrCO_3$ content increased from 0% to 6%, and then stabilized with further increase of Sr. The catalyst lifetime also enhanced significantly. The authors argued that $SrCO_3$ provided a three dimensional frame and served as an electron transfer bridge, thus enhancing the activity. The clear role of $SrCO_3$ in the system, however, remains unclear.

Despite these advances, no present catalytic system for DME production from CO_2 provides satisfactory activity, selectivity and stability. Future works should be emphasized on the effective interaction between metal and acid functional sites so that the reaction could occur sequentially. More effort should also be given to extend catalyst lifetime, resistance to poison (water and CO_2), and resistance to sintering.

Conclusions

If the conversion of CO_2 to other materials can be considered to some degree as an artificial version of nature's carbon cycle, the chemical routes from CO_2 to FA and DME cannot be industrially implemented today due to lack of efficient catalysts and process. It is important to note that these routes have not been investigated into detail over well-defined heterogeneous catalysts. The state-of-the-art in this field reveals substantial limitations and no clear insights at the molecular level have thus far been developed, hindering concrete progress. There is a clear lack of understanding of structure–reactivity correlations and of catalyst designing principles for these reactions. But in the past decade, promising advancements in the production of FA and DME from CO_2 have been made using nanoscale metal catalysts. Relevant examples already highlight the strong potential of this class of catalysts where novel solutions for the valorization of CO_2 in the future could be found thanks to more in-depth studies on better defined systems or on reaction mechanism. Thus, by taking benefit of recent knowledge and know-how in nanotechnology and nanocatalysis should lead to novel strategies in the design of efficient and more stable nanocatalysts to achieve transformation of CO_2 into FA and DME, for example by separately optimizing the metal active sites and the support. Strong research efforts are needed to achieve this goal. What is also needed is to keep in mind that harmonization is necessary to ensure a constant and dynamic balance of all things to be considered, for a sustainable and green chemistry [39]. The use of H_2 issued from green sources like water appears as a great solution to have a closed nature's carbon cycle.

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

1. • Senftle TP, Carter EA: **The holy grail: chemistry enabling an economically viable CO_2 capture, utilization and storage strategy**. *Acc Chem Res* 2017, **50**:472-475.
An interesting account that highlights the challenges that chemist must overcome to achieve the holy grail of an economically viable strategy for the capture, utilization and storage of CO_2.

2. Aresta M, Dibenedetto A, Angelini A: **Catalysis for the valorization of exhaust carbon: from CO_2 to chemicals, materials and fuels. Technologies use of CO_2**. *Chem Rev* 2014, **114**:1709-1742.

3. •• Artz J, Müller TE, Thenert K, Kleinekorte J, Meys R, Sternberg A, Bardow A: **Sustainable conversion of carbon dioxide: an integrated review of catalysis and life cycle assessment**. *Chem Rev* 2018, **118**:434-504.
A very recent analysis of the state-of-the-art of synthetic methodologies and CO_2-involving processes with the assessment of their life cycle in order to evaluate the potential to reduce the environmental footprint relative to the current petrochemical value chain.

4. Aresta M, Dibenedetto A, Angelini A: **The changing paradigm in CO_2 utilization**. *J CO_2 Util* 2013, **3–4**:65-73.

5. Chauvier C, Cantat T: **A viewpoint on chemical reductions of carbon-oxygen bonds in renewable feedstocks including CO_2 and biomass**. *ACS Catal* 2017, **7**:2107-2115.

6. Hu B, Guild C, Suib SL: **Thermal, electrochemical, and photochemical conversion of CO_2 to fuels and value-added products**. *J CO_2 Util* 2013, **1**:18-27.

7. Müller K, Brooks K, Autrey T: **Hydrogen storage in formic cid: a comparison of process options**. *Energy Fuels* 2017, **31**:12603-12611.

8. Jessop PG, Joó F, Tai CC: **Recent advances in the homogeneous hydrogenation of carbon dioxide**. *Coord Chem Rev* 2004, **248**:2425-2442.

9. Wang WH, Himeda Y, Muckerman JT, Manbeck GF, Fujita E: **CO_2 hydrogenation to formate and methanol as an alternative to photo- and electrochemical CO_2 reduction**. *Chem Rev* 2015, **115**:12936-12973.

10. Sordakis K, Tang C, Vogt LK, Junge H, Dyson PJ, Beller M, Laurenczy G: **Homogeneous catalysis for sustainable hydrogen storage in formic acid and alcohols**. *Chem Rev* 2018, **118**:372-433.

11. Bontemps S: **Boron-mediated activation of carbon dioxide**. *Coord Chem Rev* 2016, **308**:117-130.

12. Dibenedetto A, Stufano P, Nocito F, Aresta M: **Ru^{II}-mediated hydrogen transfer from aqueous glycerol to CO_2: from waste to value-added products**. *Chem Sus Chem* 2011, **4**:1311-1315.

13. •• Álvarez A, Bansode A, Urakawa A, Bavykina AV, Wezendonk TA, Makkee M, Gascon J, Kapteijn F: **Challenges in the greener production of formates/formic acid, methanol, and DME by heterogeneously catalyzed CO_2 hydrogenation processes**. *Chem Rev* 2017, **117**:9804-9838.

A recent review where the recent advances in the development of heterogeneous catalysts and processes for the direct hydrogenation of CO_2 to formate/formic acid, methanol, and dimethyl ether are discussed with special emphasis on thermodynamics and catalyst design considerations.

14. • Gunasekar GH, Park K, Jungb KD, Yoon S: **Recent developments in the catalytic hydrogenation of CO_2 to formic acid/formate using heterogeneous catalysts**. *Inorg Chem Front* 2016, **3**:882-895.

A short review dedicated to the application of heterogenized and heterogeneous catalysts for the transformation of CO_2 to formic acid.

15. Bredig G, Carter SR: **Katalytische synthese der ameisensäure unter druck**. *Ber Dtsch Chem Ges* 1914, **47**:541-545.

16. Farlow MW, Adkins H: **The hydrogenation of carbon dioxide and a correction of the reported synthesis of urethans**. *J Am Chem Soc* 1935, **57**:2222-2223.

17. Preti D, Resta C, Squarcialupi S, Fachinetti G: **Carbon dioxide hydrogenation to formic acid by using a heterogeneous gold catalyst**. *Angew Chem Int Ed* 2011, **50**:12551-12554.

18. Wiener H, Blum J, Feilchenfeld H, Sasson Y, Zalmanov N: **The heterogeneous catalytic hydrogenation of bicarbonate to formate in aqueous solutions**. *J Catal* 1988, **110**:184-190.

19. Hao CY, Wang SP, Li MS, Kang LQ, Ma X: **Hydrogenation of CO_2 to formic acid on supported ruthenium catalysts**. *Catal Today* 2011, **160**:184-190.

20. Philippot K, Serp P (Eds): *Nanomaterials in Catalysis*. Weinheim: Wiley-VCH; 2013.

21. Filonenko GA, Vrijburg WL, Hensen EJM, Pidko EA: **On the activity of supported Au catalysts in the liquid phase hydrogenation of CO_2 to formates**. *J Catal* 2016, **343**:97-105.

22. Lin W, Stocker KM, Schatz GC: **Mechanisms of hydrogen-assisted CO_2 reduction on nickel**. *J Am Chem Soc* 2017, **139**:4663-4666.

23. Gong L, Chen JJ, Mu Y: **Catalytic CO_2 reduction to valuable chemicals using NiFe-based nanoclusters: a first-principles theoretical evaluation**. *Phys Chem Chem Phys* 2017, **19**:28344-28353.

24. Nguyen LTM, Park H, Banu M, Kim KJ, Youn DH, Magesh G, Kim WY, Lee JS: **A highly active and stable palladium catalyst on a g-C_3N_4 support for direct formic acid synthesis under neutral conditions**. *Chem Commun* 2016, **52**:14302-14305.

25. Park H, Lee JH, Kim EH, Kim KY, Choi YH, Youn DH, Lee JS: **Catalytic CO_2 hydrogenation to formic acid over carbon nanotube-graphene supported PdNi alloy**. *RSC Adv* 2015, **5**:105560-105566.

26. Lee JH, Ryu J, Kim JY, Nam SW, Han JH, Lim TH, Gautam S, Chae KH, Yoon CW: **Carbon dioxide mediated, reversible chemical hydrogen storage using a Pd nanocatalyst supported on mesoporous graphitic carbon nitride**. *J Mater Chem A* 2014, **2**:9490-9495.

27. Song H, Zhang N, Zhong C, Liu Z, Xiao M, Gai H: **Hydrogenation of CO_2 into formic acid using a palladium catalyst on chitin**. *New J Chem* 2017, **41**:9170-9177.

28. Mori K, Taga T, Yamashita H: **Isolated single-atomic Ru catalyst bound on a layered double hydroxide for hydrogenation of CO_2 to formic acid**. *ACS Catal* 2017, **7**:3147-3151.

29. Upadhyay PR, Srivastava V: **Selective hydrogenation of CO_2 gas to formic acid over nanostructured Ru-TiO_2 catalysts**. *RSC Adv* 2016, **6**:42297-42306.

30. Upadhyay PR, Srivastava V: **Ionic liquid mediated in situ synthesis of Ru nanoparticles for CO_2 hydrogenation reaction**. *Catal Lett* 2017, **147**:1051-1060.

31. Qadir MI, Weilhard A, Fernandes JA, de Pedro I, Vieira BJC, Waereneborgh JC, Dupont J: **Selective carbon dioxide hydrogenation driven by ferromagnetic RuFe nanoparticles in ionic liquids**. *ACS Catal* 2018, **8**:1621-1627.

32. Umegaki T, Enomoto Y, Kojima Y: **Metallic ruthenium nanoparticles for hydrogenation of supercritical carbon dioxide**. *Catal Sci Technol* 2016, **6**:409-412.

33. Qin Z, Zhou X, Su T, Jiang Y, Ji H: **Hydrogenation of CO_2 to dimethyl ether on La-, Ce-modified Cu-Fe/HZSM-5 catalysts**. *Catal Commun* 2016, **75**:78-82.

34. Zhou X, Su T, Jiang Y, Qin Z, Ji H, Guo Z: **CuO-Fe_2O_3-CeO_2/HZSM-5 bifunctional catalyst hydrogenated CO_2 for enhanced dimethyl ether synthesis**. *Chem Eng Sci* 2016, **153**:10-20.

35. Sun K, Lu W, Wang M, Xu X: **Low-temperature synthesis of DME from CO_2/H_2 over Pd-modified CuO–ZnO–Al_2O_3–ZrO_2/HZSM-5 catalysts**. *Catal Commun* 2004, **5**:367-370.

36. Bonura G, Frusteri F, Cannilla C, Ferrante GD, Aloise A, Catizzone E, Migliori M, Giordano G: **Catalytic features of CuZnZr–zeolite hybrid systems for the direct CO_2-to-DME hydrogenation reaction**. *Catal Today* 2016, **277**:48-54.

37. Liu R, Tian H, Yang A, Zha F, Ding J, Chang Y: **Preparation of HZSM-5 membrane packed CuO–ZnO–Al_2O_3 nanoparticles for catalysing carbon dioxide hydrogenation to dimethyl ether**. *Appl Surf Sci* 2015, **345**:1-9.

38. Zhang X, Wang M, Yang A, Kong C, Zhai Y: **Effect of $SrCO_3$ additive on CuZnAl/HZSM-5 catalyst property for the direct DME synthesis**. *Water Air Soil Pollut* 2015, **226**:378.

39. Horvath IT: **Introduction to sustainable chemistry**. *Chem Rev* 2018, **118**:369-371.